

# Microstructures and Vortex Pinning in MOD and PVD-BaF<sub>2</sub> *ex-situ* YBCO Films on RABiTS™

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# Overview

- ❖ Baseline MOD and PVD-BaF<sub>2</sub> *ex-situ* YBCO films on RABiTS™.
  - ↳ Characteristic microstructures
  - ↳ Baseline pinning microstructure
- ❖ Microstructure modifications for changing and understanding the pinning characteristics in *ex-situ* YBCO films.
  - ↳ Alternative heat treatments to baseline samples
  - ↳ RE<sub>2</sub>O<sub>3</sub> additions (RE= Ho, Er, Pr, Eu, Yb, Sm)
  - ↳ Excess Y<sub>2</sub>O<sub>3</sub> additions (PVD-BaF<sub>2</sub> Ron Feenstra-ORNL)

**Tool Kit:** Electron Microscopy, Raman, XRD, self-field J<sub>c</sub>(T), angular anisotropy measurements of J<sub>c</sub>(H,T,Θ), comparisons to *in-situ* (pulsed laser deposition - PLD) YBCO films.

The same RABiTS™-based architecture is used for research and scale-up.

❖ WDG research directly tied to AMSC scale-up efforts.

❖ YBCO films

➤ 0.4 to 1.7  $\mu\text{m}$  for MOD- $\text{BaF}_2$  (Metal-Organic Deposition of precursors)

➤ High  $J_c$

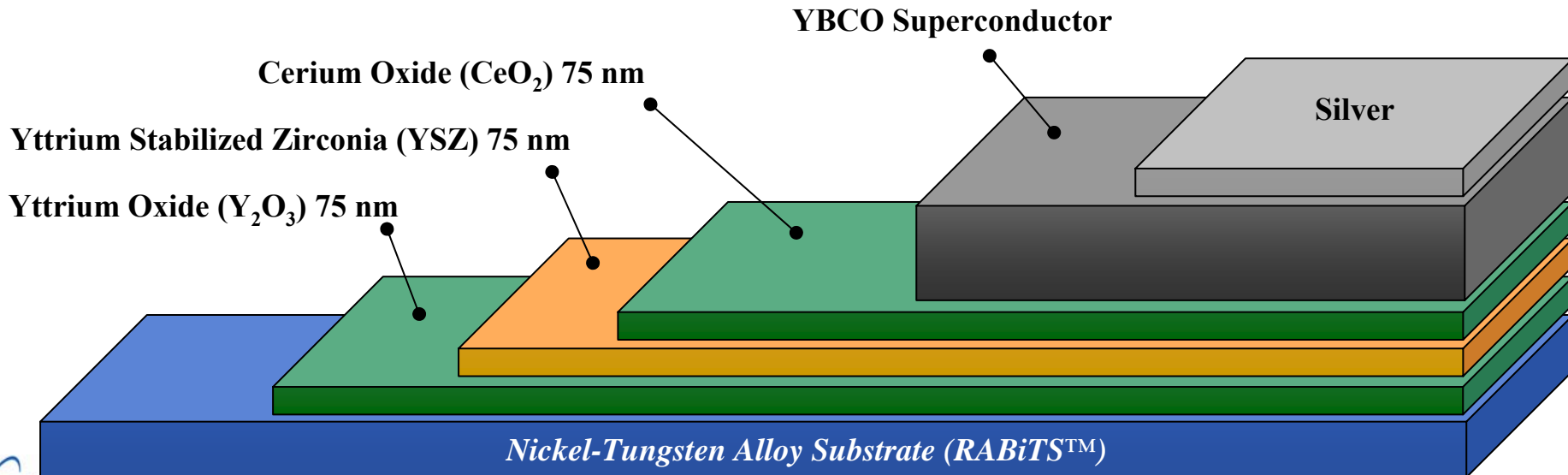
➤ Process to be scaled commercially

➤ 0.1 to 3  $\mu\text{m}$  for PVD- $\text{BaF}_2$  (Physical Vapor Deposition of precursors)

➤ High  $J_c$

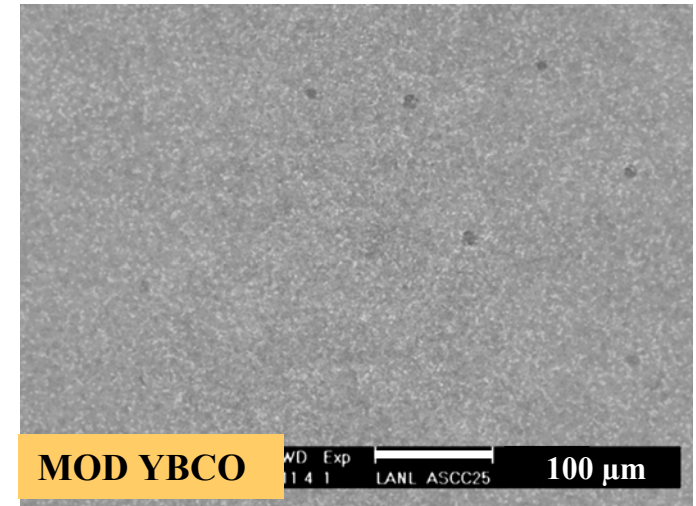
➤ Similar conversion process to MOD

➤ Flexible tool for investigating a wide range of films



The MOD YBCO films produced at American Superconductor are macroscopically uniform.

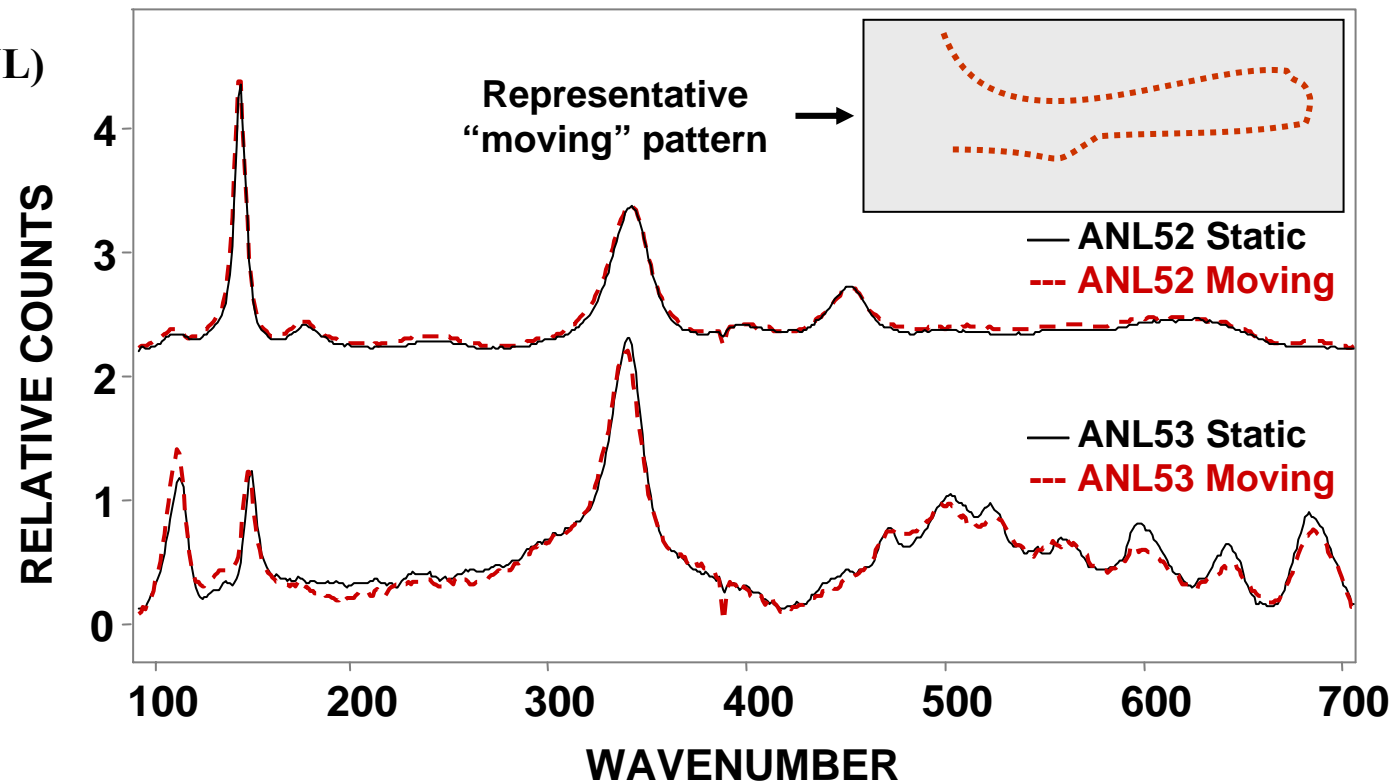
- ❖ SEM analysis shows few surface defects.
- ❖ Essentially no difference in the Raman spectra with regards to individual spectra and spectra averaged over many spots.



### Raman - Vic Maroni (ANL)

ANL52 → REBCO  
(RE = 100% Er),  
 $I_c = 120 \text{ A/cm-w}$

ANL53 → REBCO  
(RE = 50% Y and 50% ER)  
 $I_c = 150 \text{ A/cm-w}$



At the microscopic level, *ex-situ* (MOD, PVD) and *in-situ* (PLD) YBCO films have characteristically different microstructures.

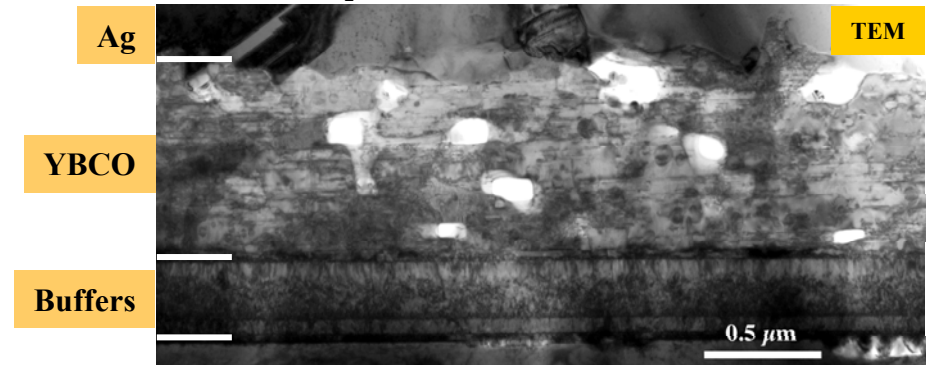
❖ Characteristic features of *ex-situ* YBCO films (MOD and PVD).

- Layered microstructure
- Mostly non-coherent inclusions
- Porosity
- Grain boundary meandering and overgrowth

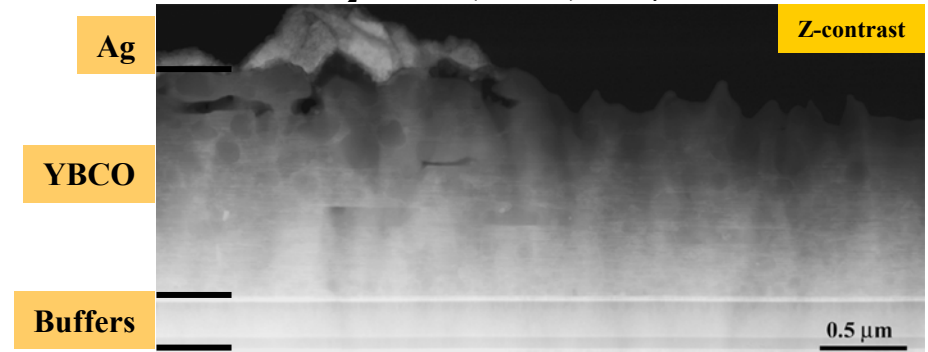
❖ Different YBCO film processes for high- $J_c$  coated conductors.

- MOD-BaF<sub>2</sub>: **AMSC**  
3.6 MA/cm<sup>2</sup> 1.0  $\mu$ m
- PVD-BaF<sub>2</sub>: **ORNL**  
2.8 MA/cm<sup>2</sup> 1.1  $\mu$ m  
2.3 MA/cm<sup>2</sup> 1.7  $\mu$ m
- PLD-IBAD MgO: **LANL**  
4.1 MA/cm<sup>2</sup> 1.2  $\mu$ m

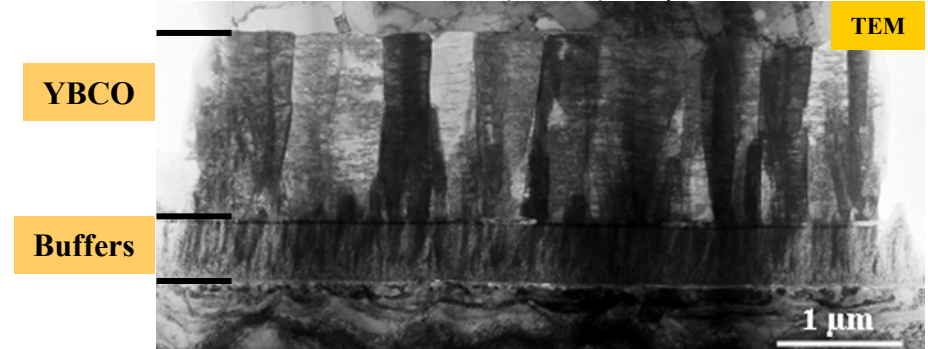
MOD-BaF<sub>2</sub> YBCO (AMSC) 0.8  $\mu$ m YBCO film



PVD-BaF<sub>2</sub> YBCO (ORNL) 1.25  $\mu$ m YBCO film

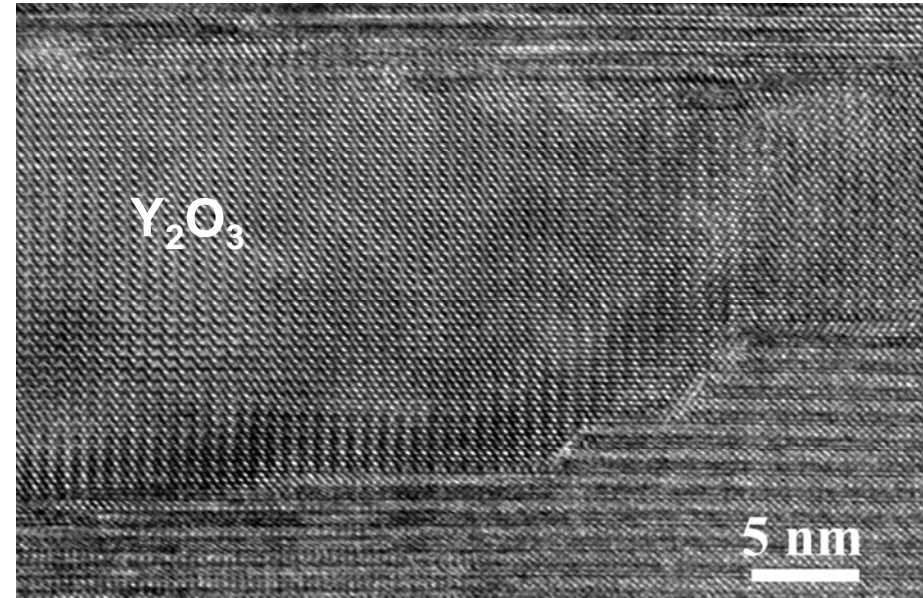


PLD YBCO/ IBAD YSZ (LANL) 1.5  $\mu$ m YBCO film



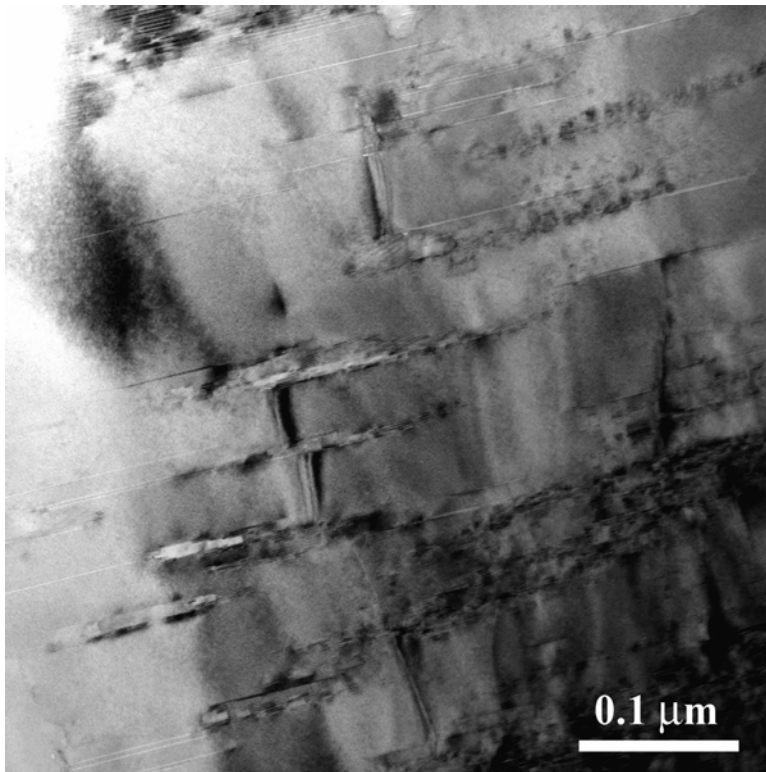
Stoichiometric *In-situ* PLD YBCO films have a columnar structure with coherent precipitates and a low density of planar defects.

- ❖ c-axis aligned defects, (grain boundaries, dislocations, anti-phase boundaries) for correlated  $J_c(H//c)$  pinning.



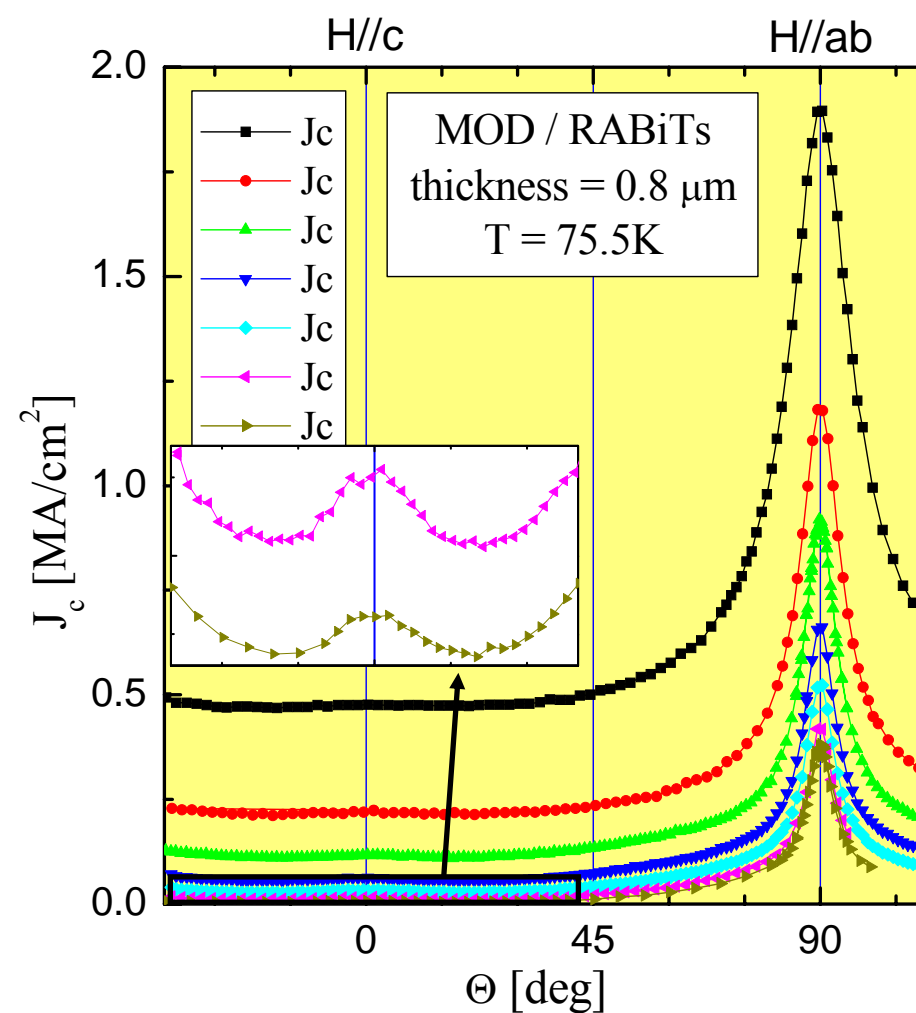
- ❖ Comparisons between the *in-situ* and *ex-situ* films are a useful tool for understanding flux pinning in ex-situ YBCO films.

LANL 1.5  $\mu m$  PLD YBCO on IBAD MgO

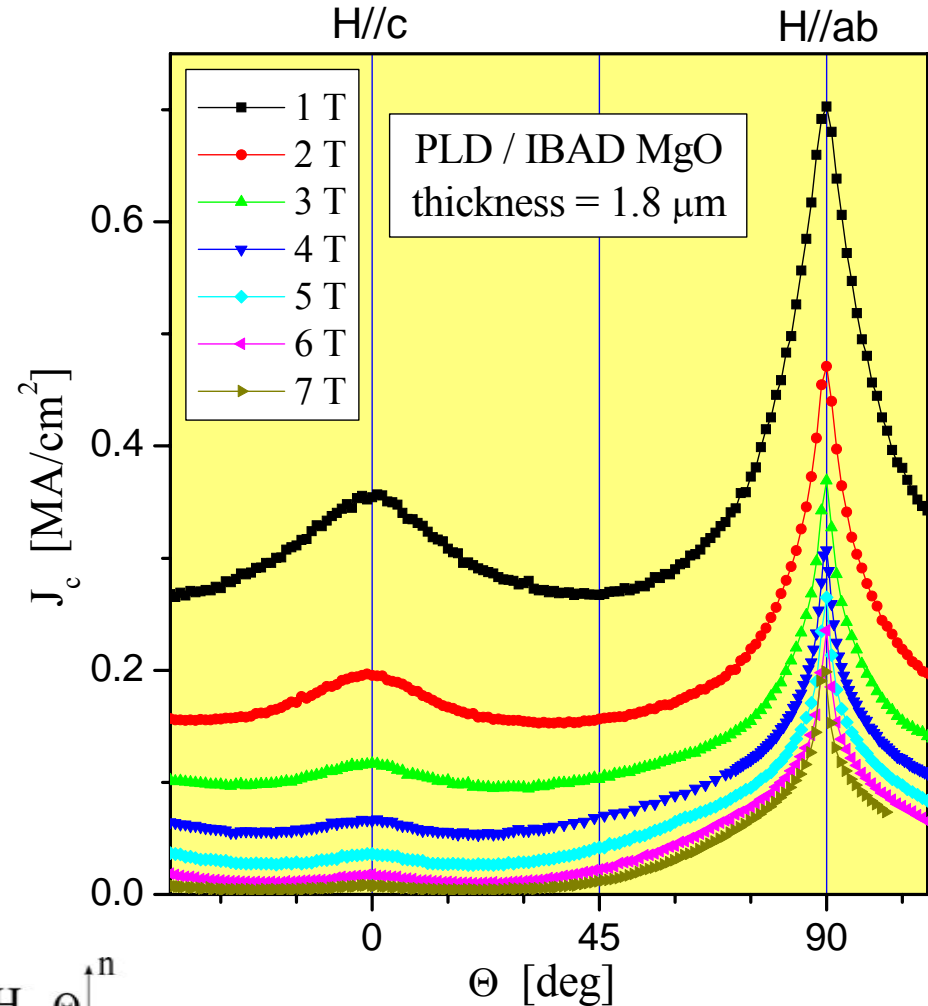


B. Maiorov et al, APL **86** 132504 (2005)

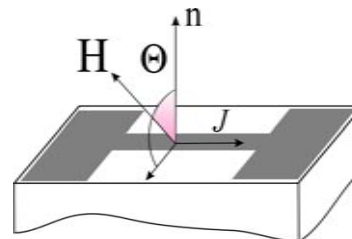
The  $J_c$  angular anisotropy measurements on baseline *ex-situ* and *in-situ* films show distinct differences. (Leonardo Civale -Peer Review 2004).



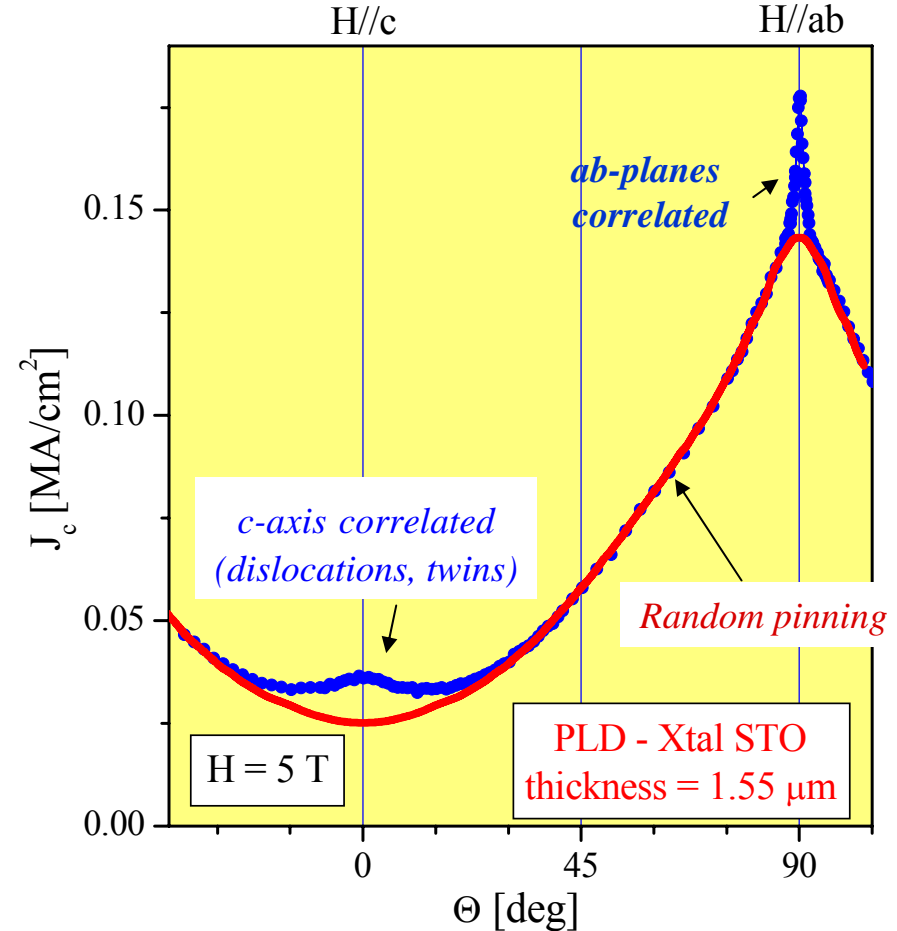
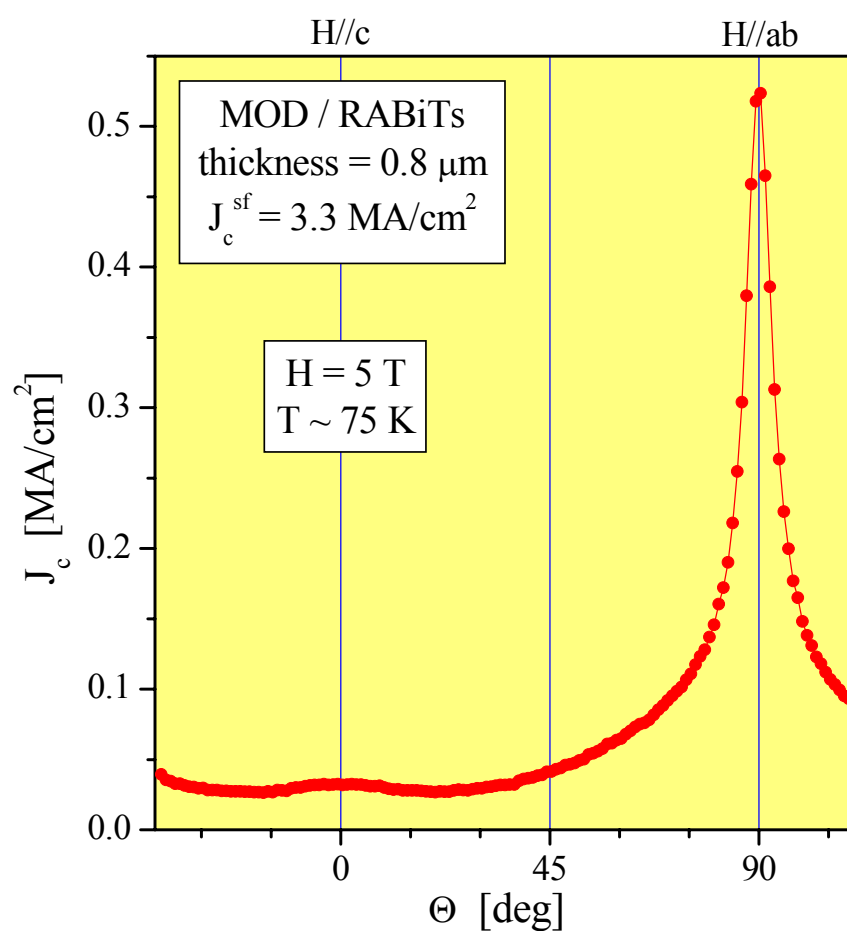
MOD: small c-axis peak,  
large ab-plane peak



PLD: large c-axis peak,  
small ab-plane peak



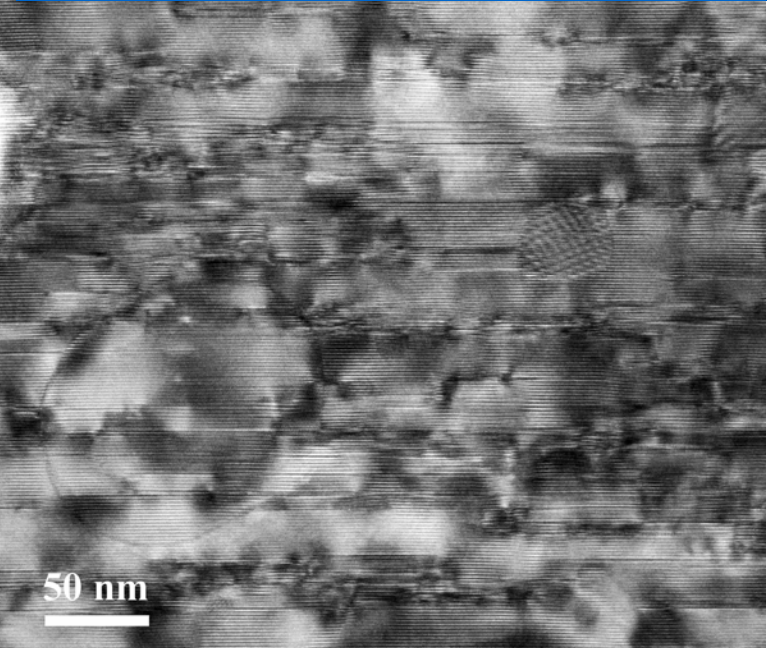
In MOD films there is no clear separation between random and ab-plane correlated pinning regimes. (Leonardo Civale -Peer Review 2004)



**Pinning in baseline MOD films is strongly dominated by ab-plane correlated defects. (What are those defects?)**

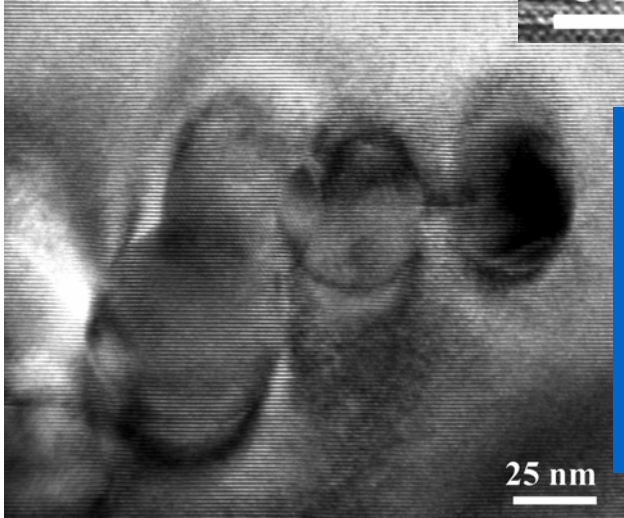
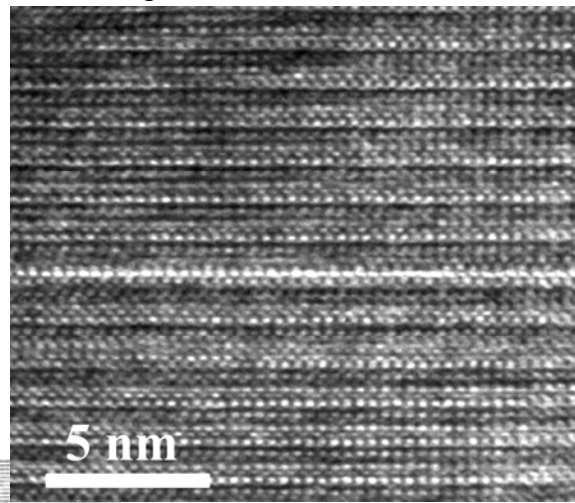
Baseline AMSC MOD *ex-situ* YBCO films are characterized by defects of various types and length scales.

*Hypothesis: Y-124 intergrowths are responsible for improved pinning (correlated pinning) for  $J_c(H\parallel ab)$ .*



Y123 11.7 Å

Y124 13.7 Å x2



Low density of non-coherent inclusions with strain fields. (Hypothesis: Correlated defect for  $H\parallel c$  pinning?)



Variable porosity  
Film tilting  
Colony structure

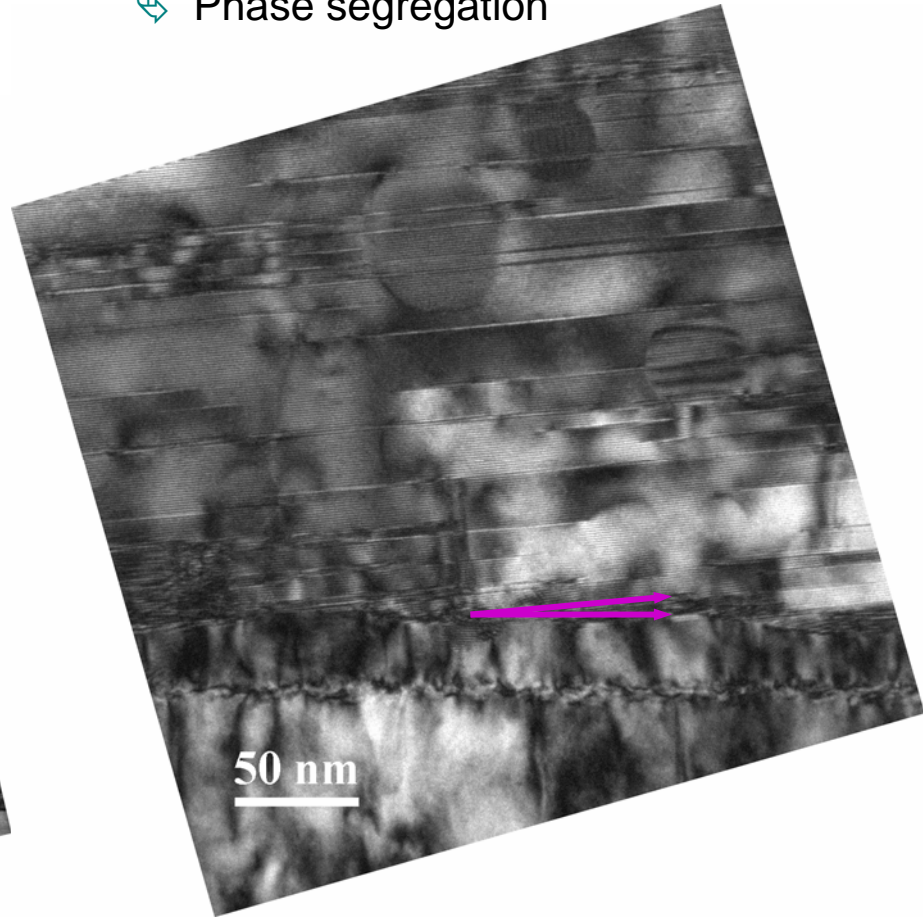
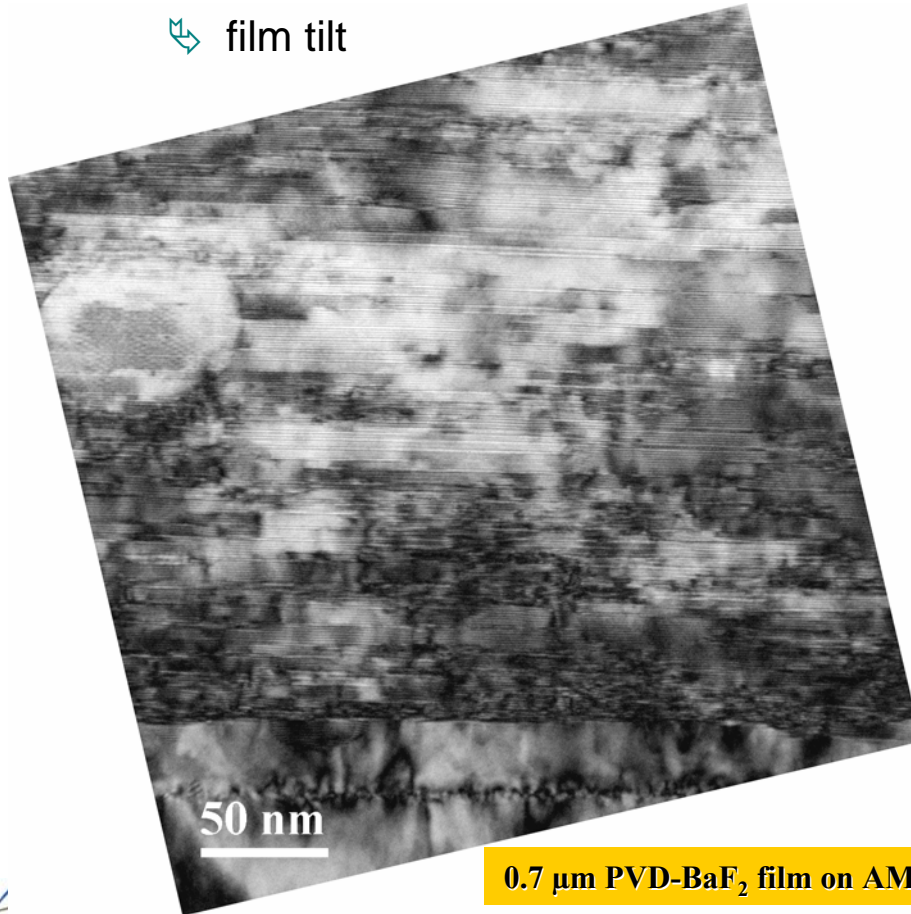
At the microscopic level, there are point-to-point variations in the microstructure of the *ex-situ* (both PVD and MOD) YBCO films.

❖ Structural variations

- ✎ porosity
- ✎ planar defects
- ✎ sub-grain structure
- ✎ film tilt

❖ Chemistry variations

- ✎ Second phase distributions
- ✎ Phase segregation



0.7 μm PVD-BaF<sub>2</sub> film on AMSC RABiTS

Microstructural variants in the MOD and PVD-BaF<sub>2</sub> YBCO films can occur due to changes in the amount of liquid phase during conversion.

❖ Phase segregation

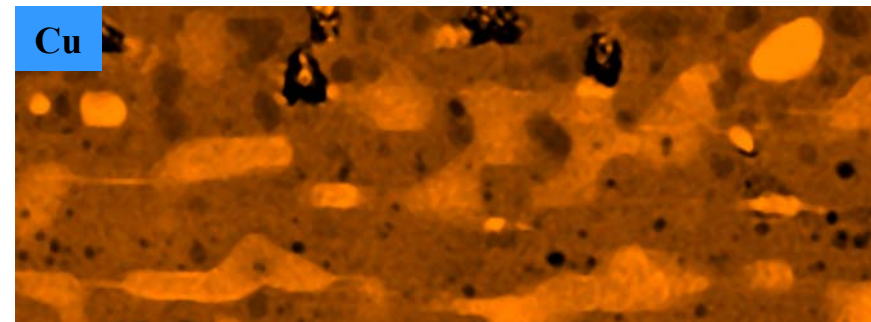
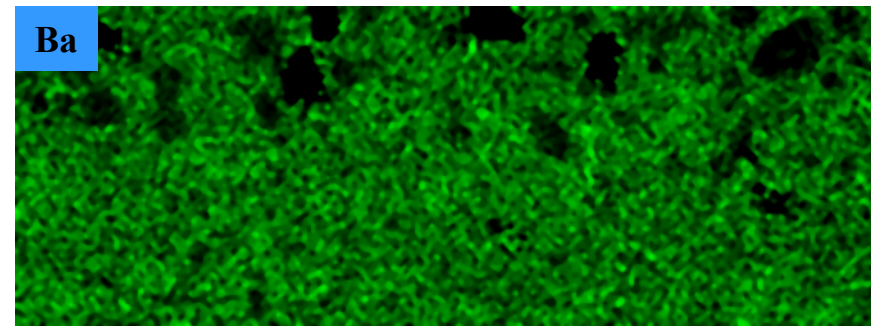
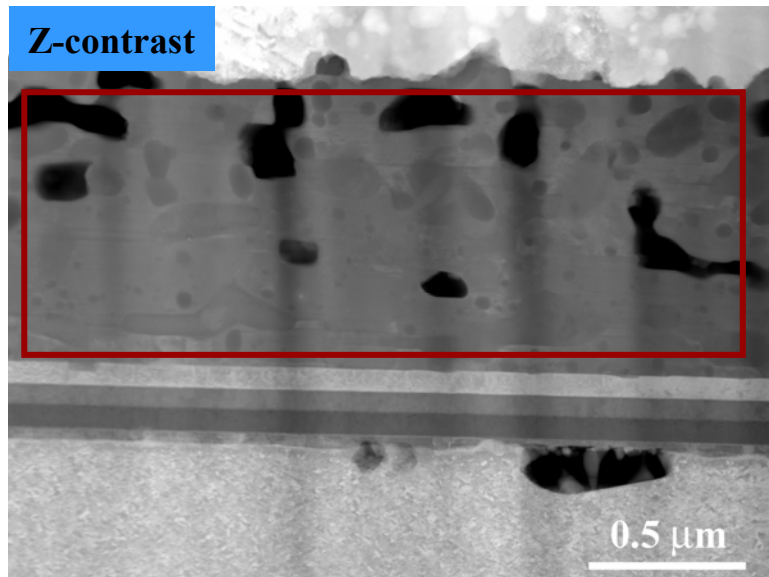
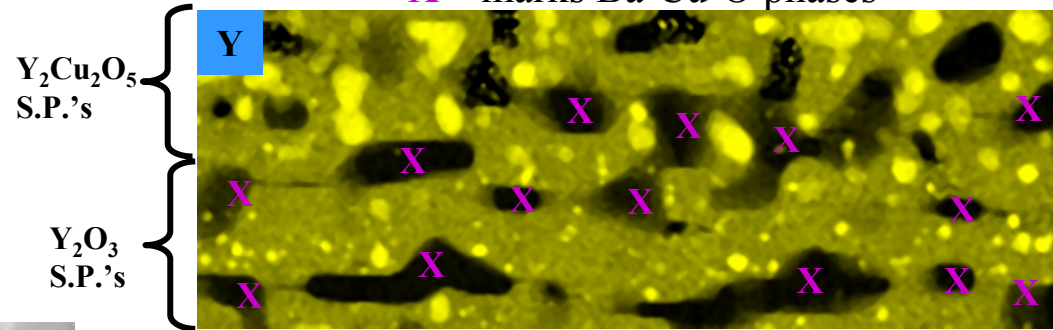
➤ PVD-BaF<sub>2</sub> research led to the understanding of several *ex-situ* microstructure variants. (Terry Holesinger - Peer Review 2004)

AMSC 0.8  $\mu\text{m}$  MOD YBCO  
Research sample processed in scale-up furnace  
 $I_c = 264 \text{ A/cm-w}$

*Still room for improvement!*

Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>, CuO, Y<sub>2</sub>O<sub>3</sub>, and Ba-Cu-O

X – marks Ba-Cu-O phases



Long-length AMSC coated conductors successfully produced with the same basic high- $J_c$  *ex-situ* YBCO structure as found in WDG research samples.

4 cm-wide long-length  
conductor  
0.8  $\mu\text{m}$  YBCO  
 $I_c = 214 \text{ A/cm-w}$

Y124 Planar Defects

100 nm

Z-contrast

Inclusions

0.25  $\mu\text{m}$

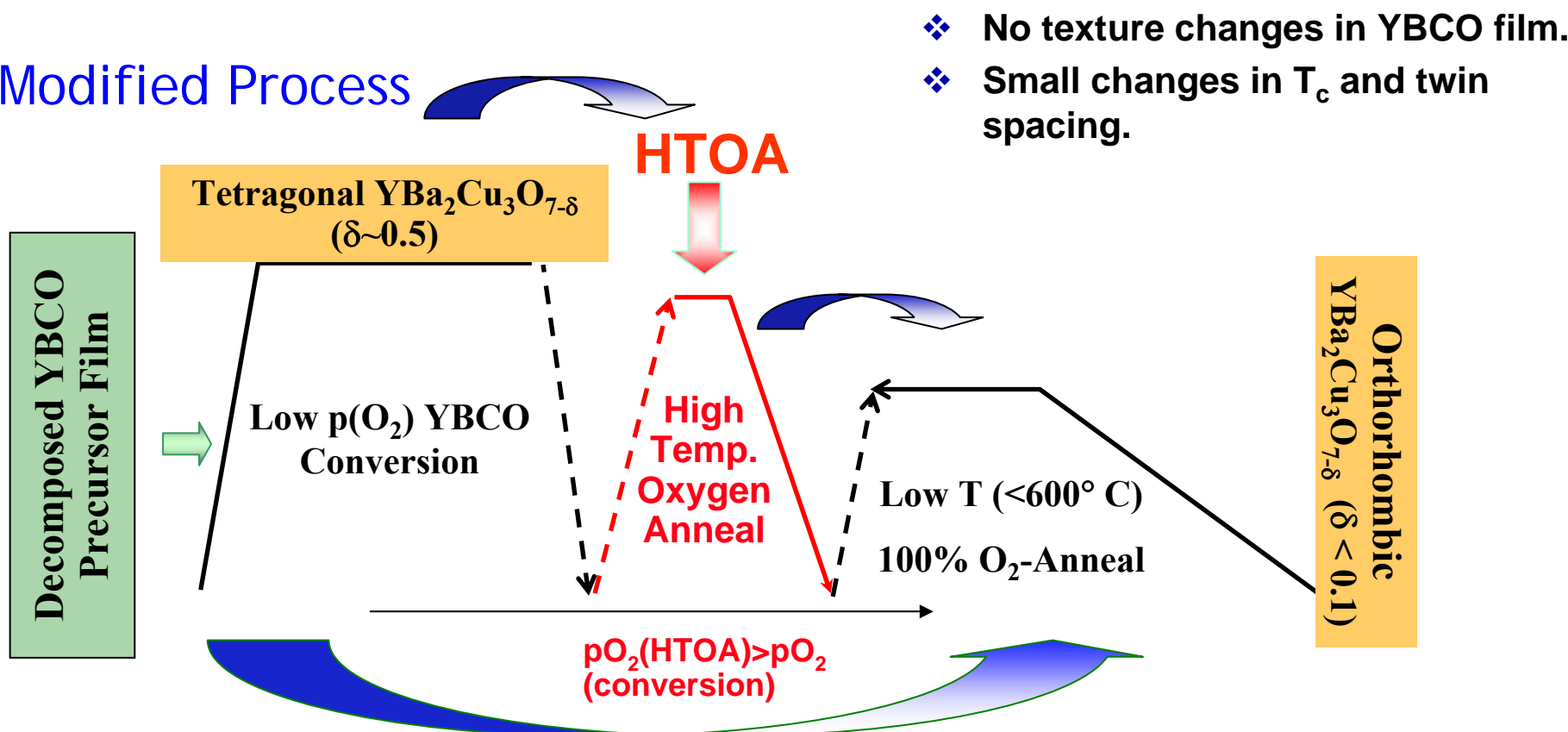
Variable Porosity  
Film tilting  
Colony structure

Bright Field STEM

1  $\mu\text{m}$

Vortex pinning in baseline MOD *ex-situ* YBCO films can be changed by modifying the heat treatment schedule.

Modified Process



- ❖ No texture changes in YBCO film.
- ❖ Small changes in  $T_c$  and twin spacing.

Baseline Process

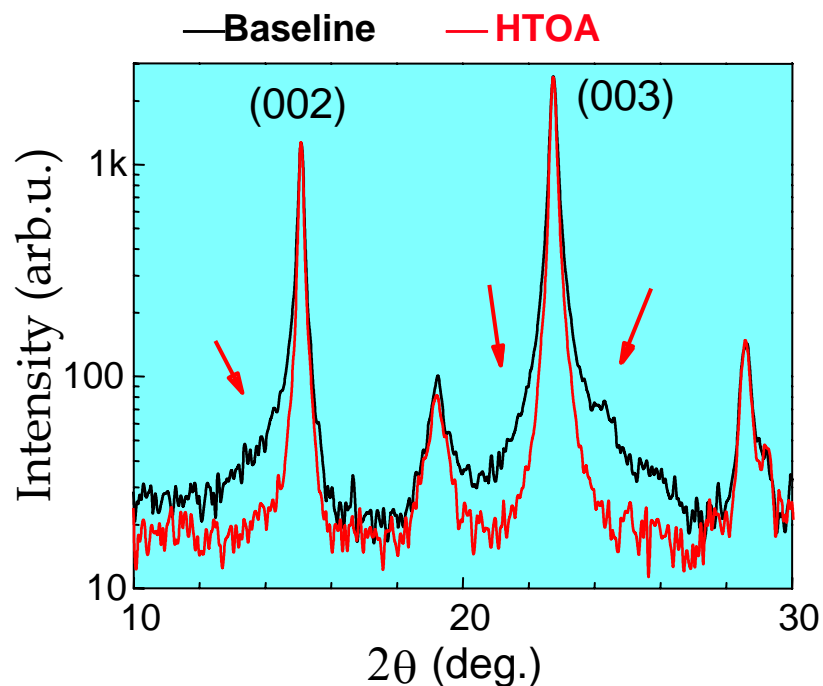
Initial Development – X. Li (AMSC) → TEM, angle-dependent  $J_c$  (LANL)  
→ TEM, Raman, XRD (ANL)  
→ XRD, angle-dependent  $J_c$  (ORNL)

The HTOA generates a c-axis peak that resembles the PLD films. What are the c-axis correlated defects?

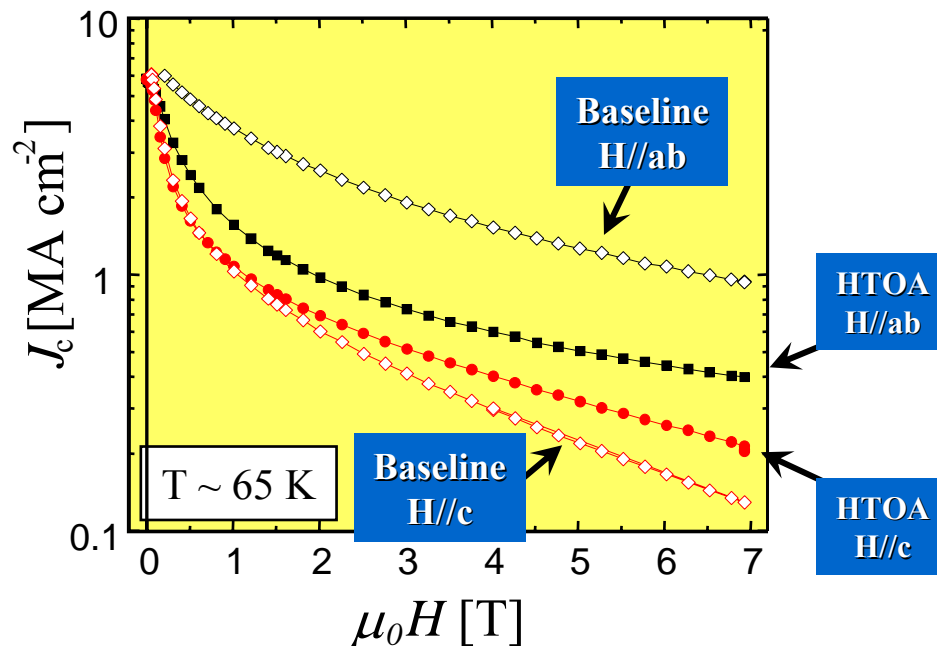
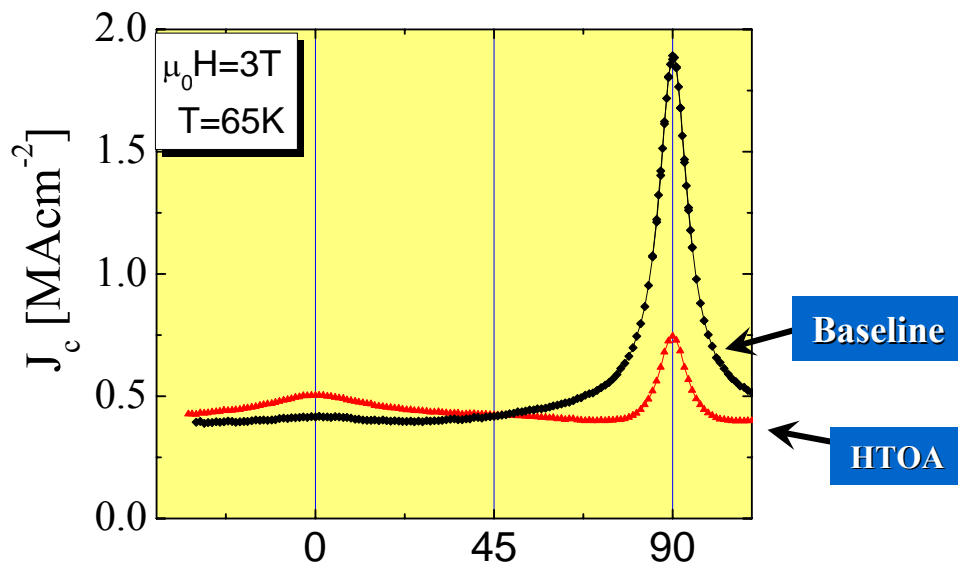
- ❖ XRD suggests a reduction in the Y-124 intergrowth density.
- ❖  $T_c$  and twin spacing changes with HTOA.

↗ 91.5K and 54.2 nm (baseline)

↗ 88 K and 77.3 nm (HTOA)



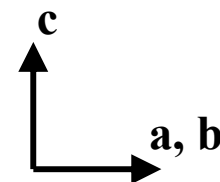
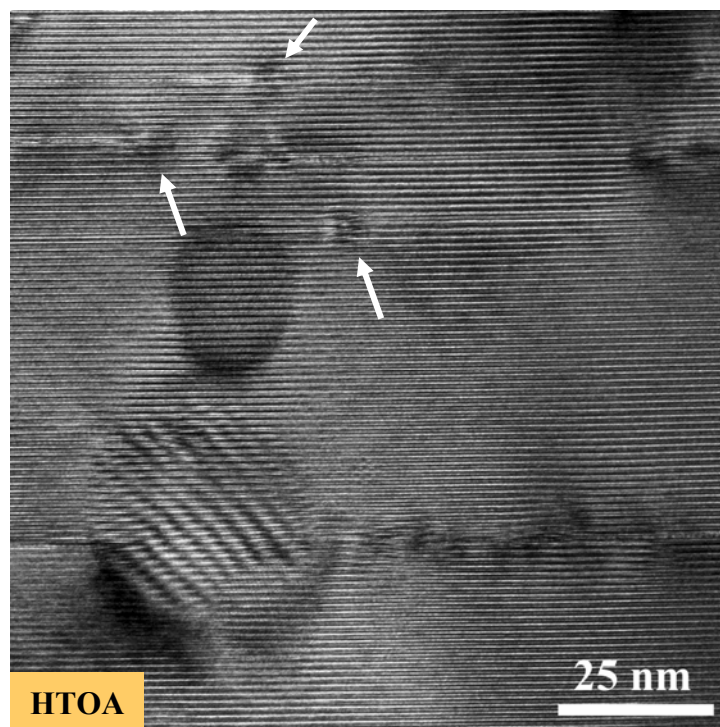
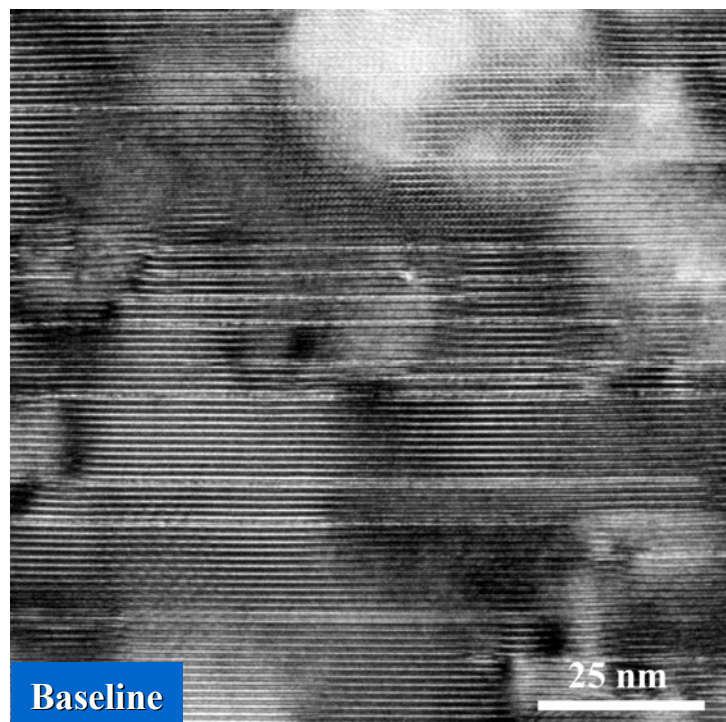
Xiaoping Li et al. AMSC



Leonardo Civale and Boris Maiorov (LANL)

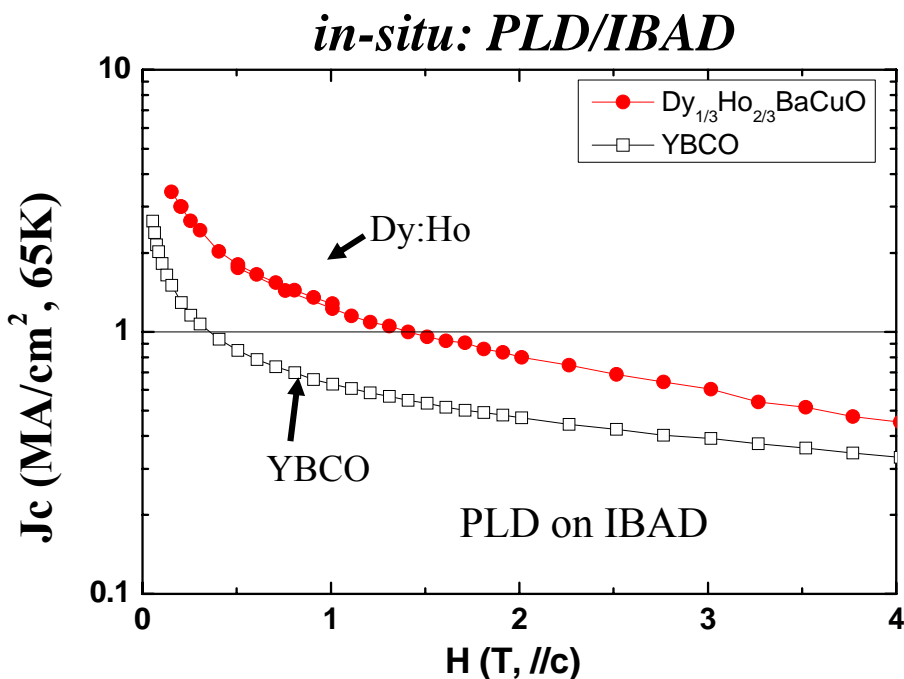
The decrease in the angular  $I_c$  anisotropy also correlates to TEM observations of a reduction in the density of Y124 planar intergrowths.

- ❖ The Y124 planar defects that end within a YBCO grain give rise to stacking faults, anti-phase boundaries, and localized strain that tend to align in the c-axis direction.

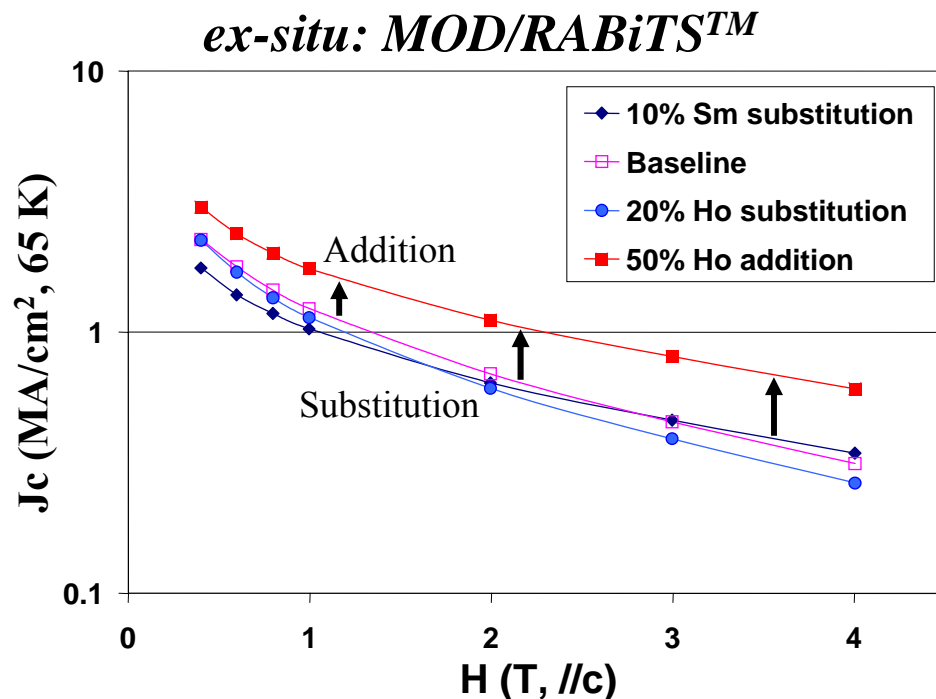


*The change in microstructure and pinning characteristics with the HTOA provides additional evidence for the Y-124 ab-plane correlated pinning effect.*

A wide variety of rare earth substitutions ( $Y_{1-x}RE_x$ ) and additions ( $Y_1RE_x$ ) in MOD *ex-situ* films studied at AMSC for pinning enhancements.



L. Civale, J. Driscoll et al., LANL,  
2004 DOE peer review



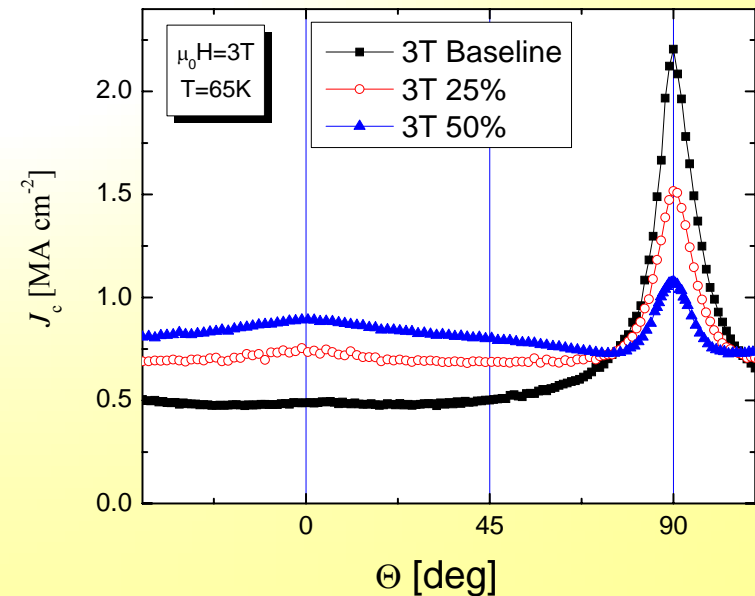
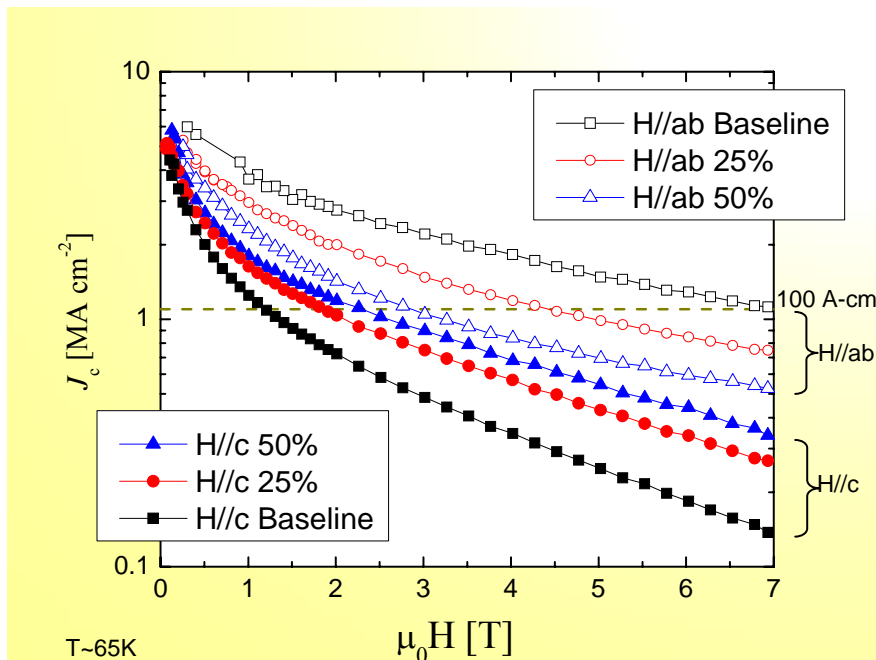
Yibing Huang et al., AMSC - new results

*In contrast to earlier PLD data, minimal  $J_c(H//c)$  increase by rare earth substitution in MOD, but significant increase of in-field  $J_c(H//c)$  by additions.*

Substantial improvements for  $J_c(H//c)$  were found for  $\text{Er}_2\text{O}_3$  additions up to the level of 50% ( $\text{Y}_1\text{Er}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_y$ ).

- ❖ Little effect on  $J_c(\text{self-field})$
- ❖ Overall increase in  $J_c(H//c)$  at the expense of  $J_c(H//ab)$
- ❖ What are the changes in the pinning microstructure?

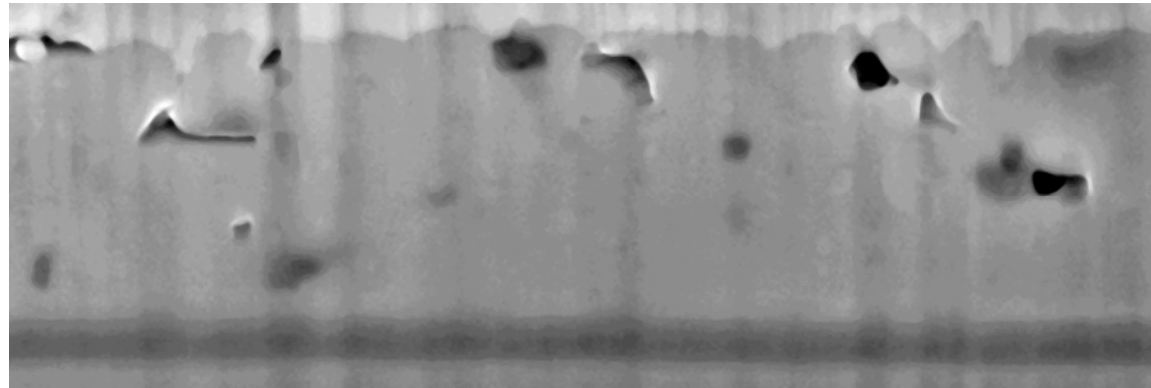
		$\underline{I_c}(\text{sf}, 75\text{K})$
Baseline	$(\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_y)$	= 250 A/cm
25%Er	$(\text{Y}_1\text{Er}_{0.25}\text{Ba}_2\text{Cu}_3\text{O}_y)$	= 260 A/cm
50%Er	$(\text{Y}_1\text{Er}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_y)$	= 260 A/cm



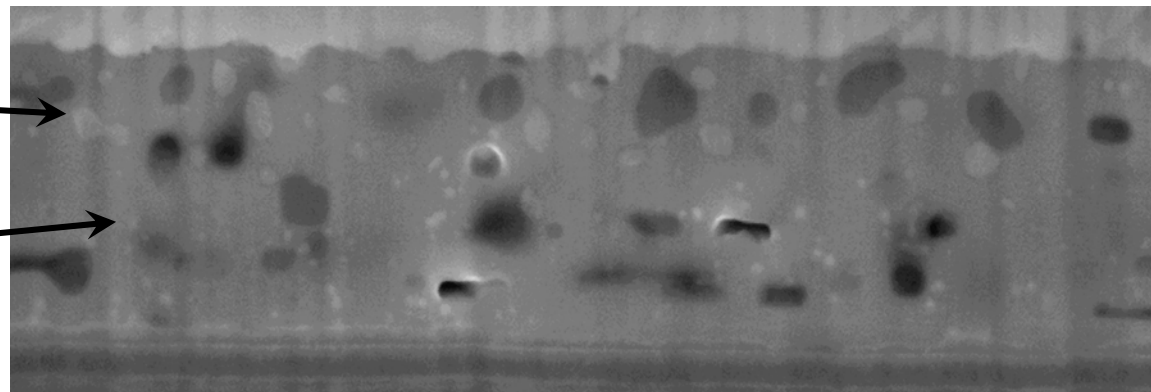
Same trends in  $J_c(H, \Theta)$  at 65K and 75K

Leonardo Civate and Boris Maiorov (LANL)

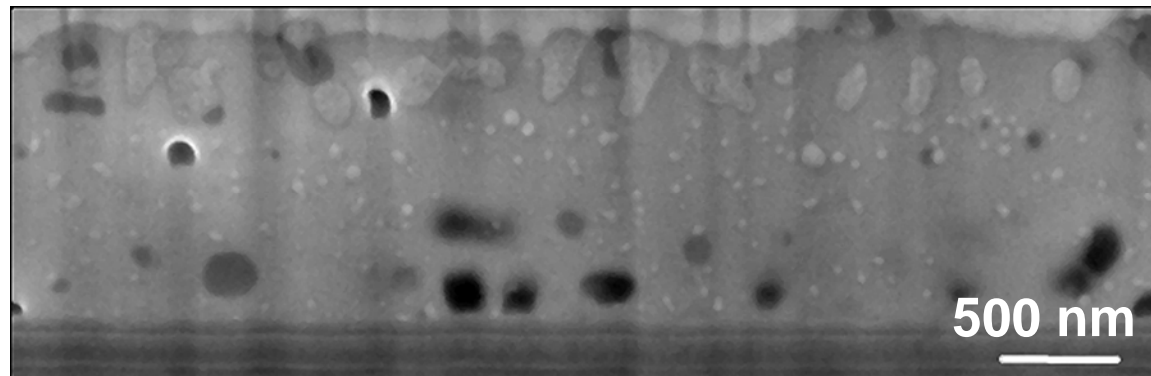
The  $\text{Er}_2\text{O}_3$  additions produced increasing amounts of  $(\text{Y},\text{Er})_2\text{O}_3$  and  $(\text{Y},\text{Er})_2\text{Cu}_2\text{O}_5$  inclusions in the AMSC *ex-situ* MOD films.



0% Er



25% Er



50% Er

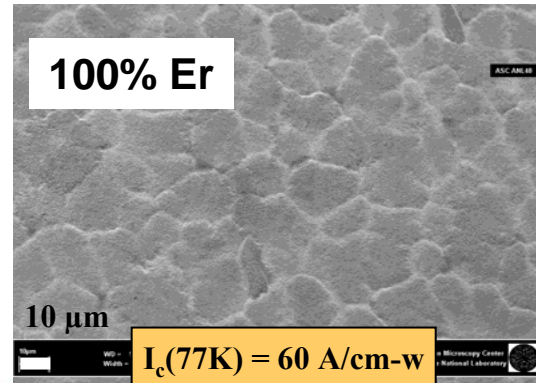
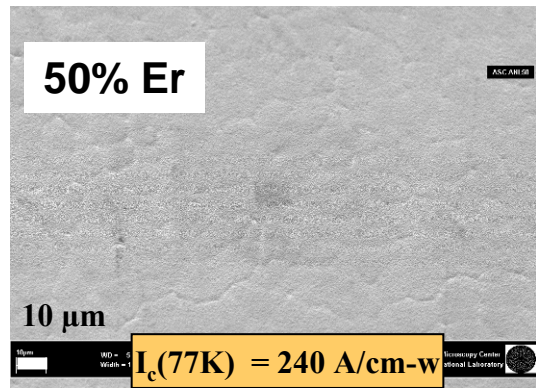
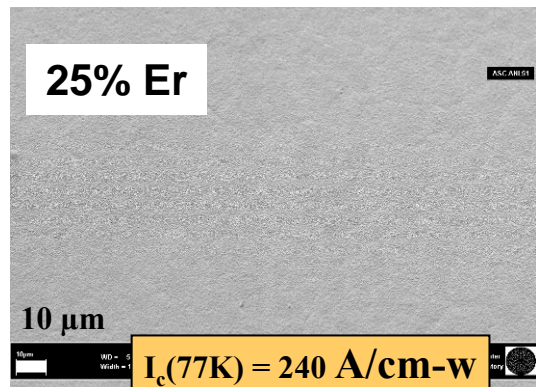
$(\text{Y},\text{Er})_2\text{Cu}_2\text{O}_y$

$(\text{Y},\text{Er})_2\text{O}_3$

FIB - Dean Miller (ANL)

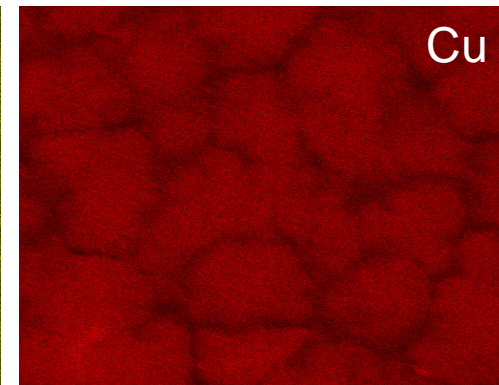
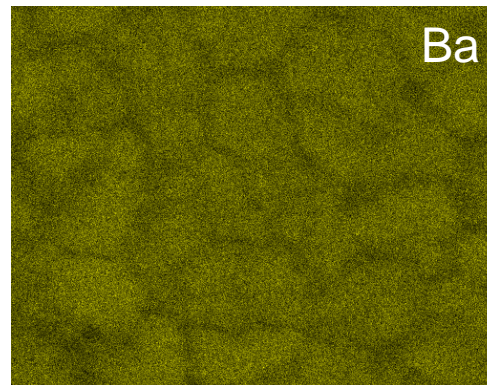
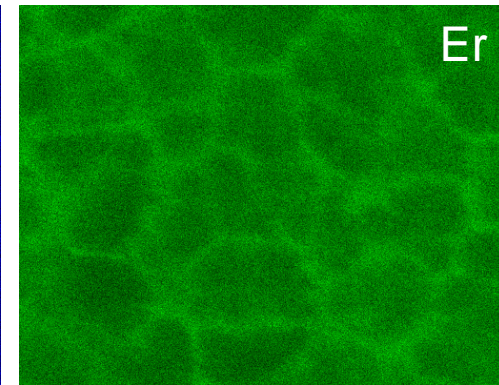
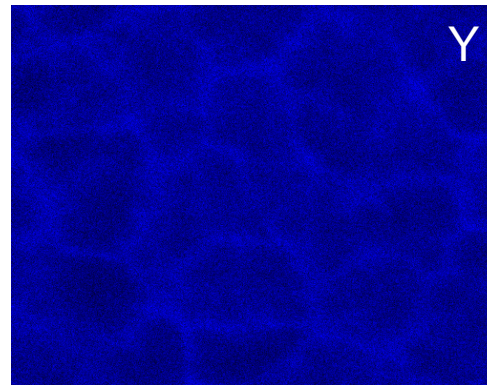
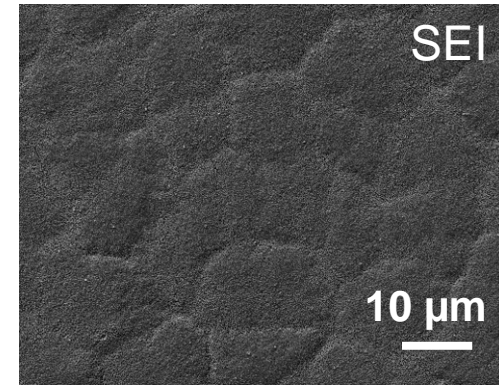
500 nm

A limit to the Er additions is reached when grain boundary segregation of the rare earths significantly reduces  $J_c$ .

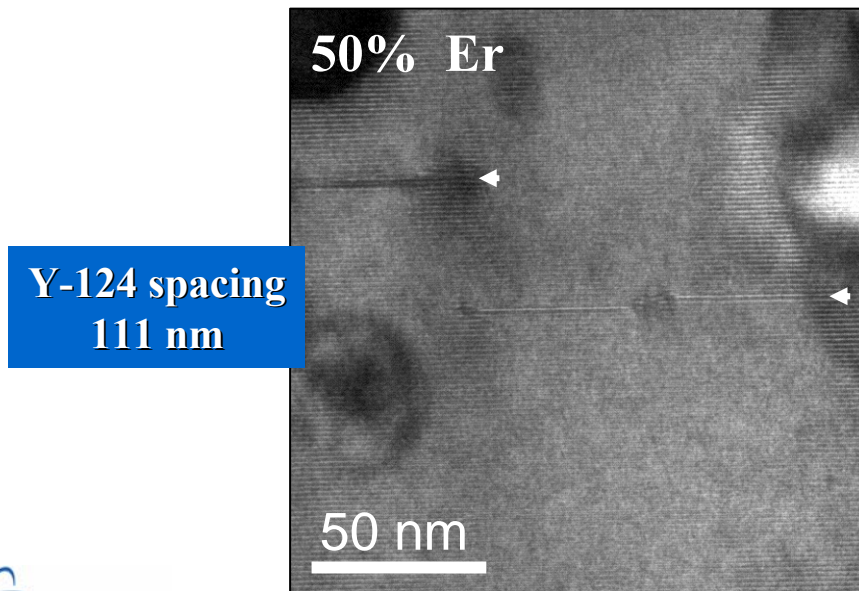
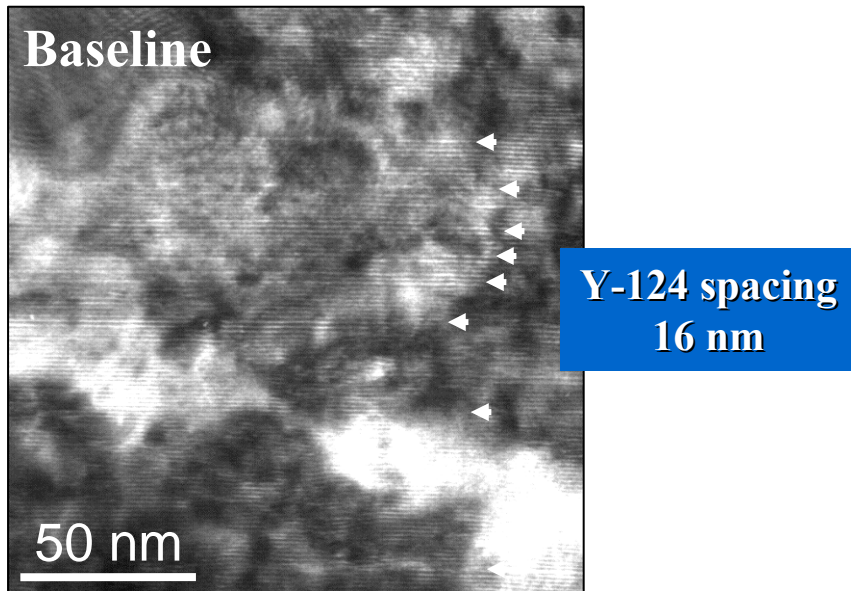


120 μm

SEM - Dean Miller (ANL)

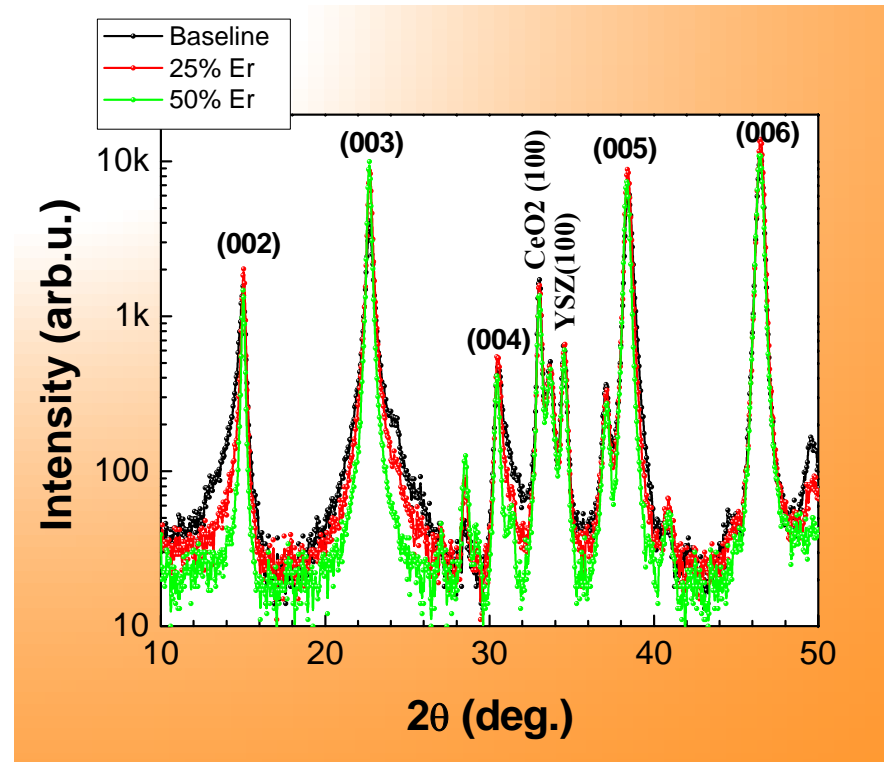


The  $\text{RE}_2\text{O}_3$  additions increase the density of the inclusions while significantly reducing the density of the ab planar intergrowths.



TEM -Dean Miller (ANL)

- ❖ Reduced peak broadening with increasing  $\text{Er}_2\text{O}_3$  additions.
- ❖ Additional support for hypothesis that H||ab correlated pinning is due to ab (Y-124) intergrowths.

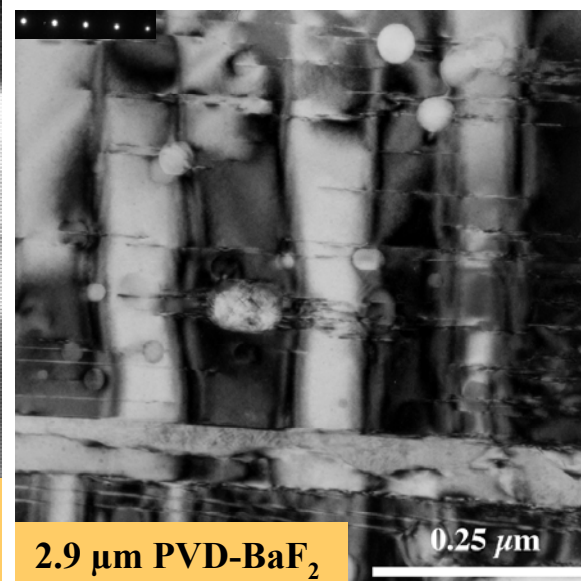
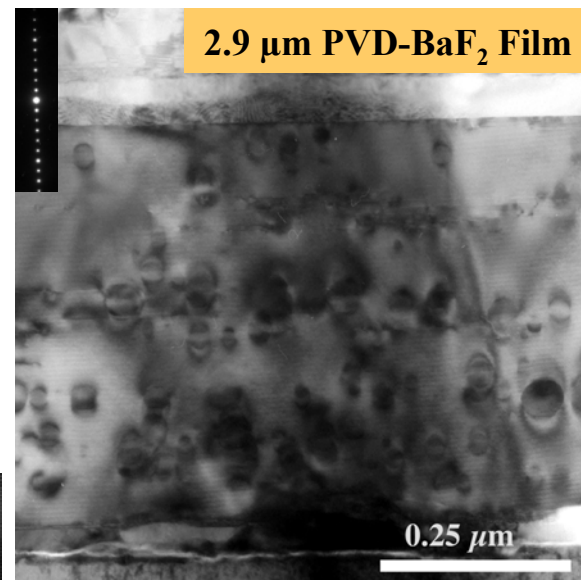
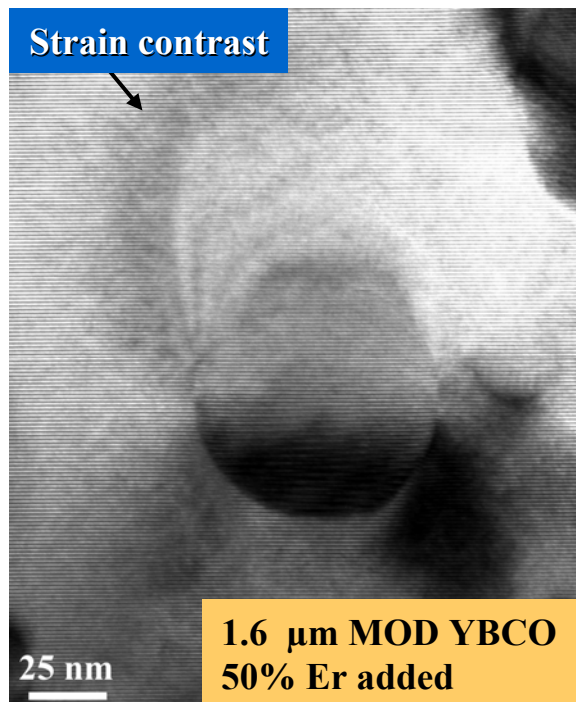
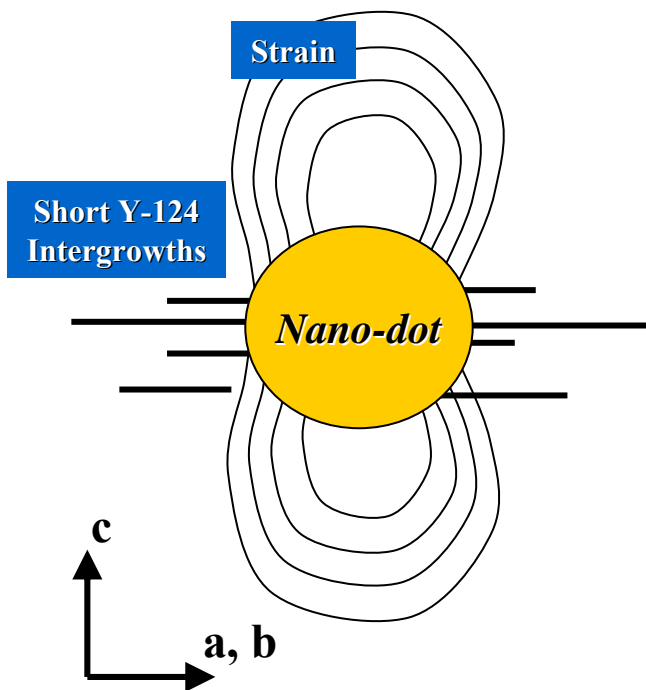


Xiaoping Li *et al.* (AMSC)

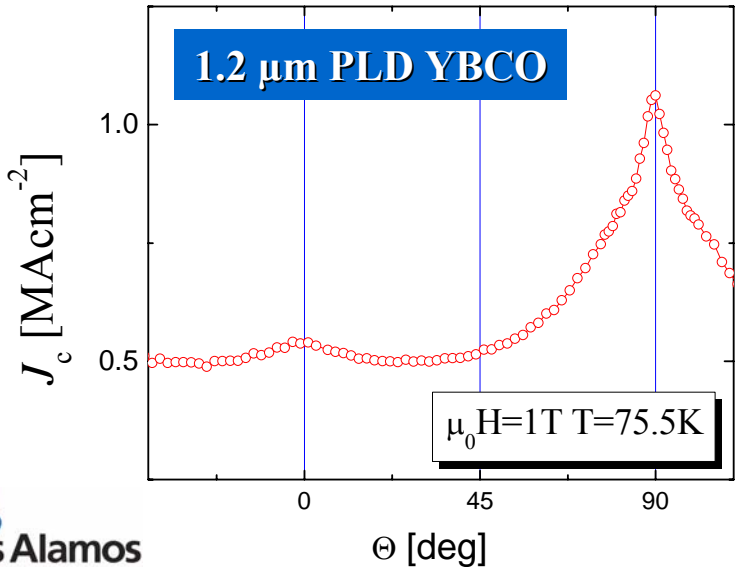
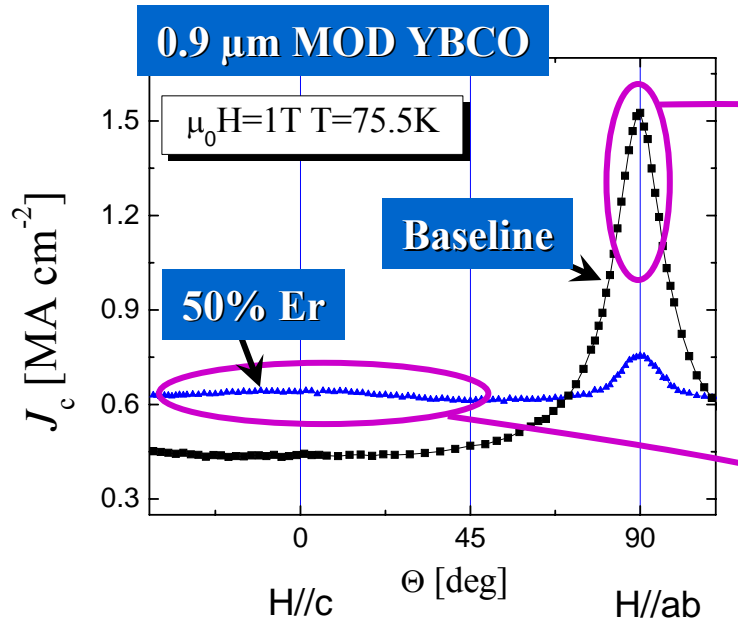
The extended defect structure around the inclusions defines a pinning structure that is much larger than the precipitate itself.

- ❖ Extended nanodot structure acts like splayed defects rather than c-axis aligned line defects in stoichiometric PLD YBCO films.

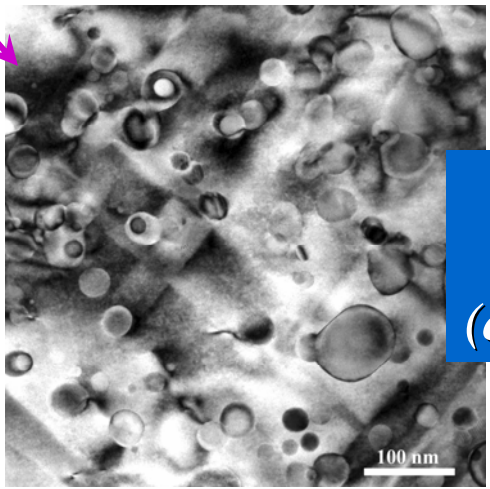
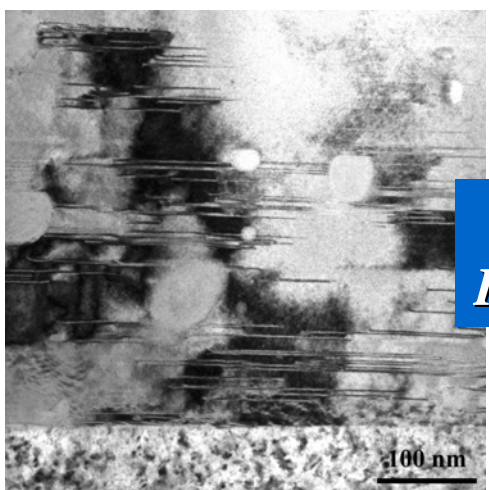
## Defect Model



Measurements of  $J_c(H, \Theta, T)$  for the 50% Er MOD YBCO film show a much broader peak centered around  $H \parallel c$  compared to standard PLD YBCO film.



❖ Considering all the data to date, we can correlate specific microstructures with specific characteristics of  $J_c(H, \Theta, T)$ .



## Summary

- ❖ Microstructural and electrical characterizations were used to highlight the differences in the structure-property relationships of *ex-situ* (lamellar structure) and *in-situ* (columnar structure) YBCO films.
- ❖ Characterizations of baseline,  $\text{RE}_2\text{O}_3$  additions, and HTOA AMSC MOD YBCO films suggest that the Y124 intergrowths are the dominant ab-plane correlated pinning defect in baseline *ex-situ* YBCO films.
- ❖ For improved  $J_c(H||c)$  pinning, *ex-situ* and *in-situ* YBCO films differ significantly in their underlying pinning mechanisms - Nanodots through  $\text{RE}_2\text{O}_3$  additions are best for *ex-situ*  $J_c(H//c)$ .

***Understanding the thin film processes of ex-situ MOD YBCO films in the WDG has helped AMSC accelerate its scale-up efforts.***